Optical Properties of Poly Vinyl Chloride PVC Films Irradiated with Beta and Gamma –Rays

Bushra A. Hasan[1], Muna A. Saeed[2] and Ahmad A. Hasan[3]
University of Baghdad, College of Science, Department of Physics
[1]mail: bushra_abhasan@yahoo.com
[3]mail: ahmadabhasan27@yahoo.com

Abstract

The effect of β and γ radiation on optical constants and the optical energy gap E_g of polyvinyl chloride PVC films casted with different thickness is presented. On the basis of quantitative analysis of obtained data, the calculated refractive index n, extinction coefficient k, real and imaginary parts of dielectric constants ε_1, and $\varepsilon_2$are found to increases with irradiation and thickness. The results show the effect of γ radiation on n valued is thickness independent while that for β radiation is thickness dependent, while k, ε_1, and ε_2 are found radiation and thickness dependent. The optical energy gap E_g values of unirradiated and irradiated PVC samples are found to change in contrast manner with that of the optical activation energy E_e .The results are discussed on the basis of the radiation induced crosslinking of PVC samples.

Keywords: polyvinyl chloride; Gamma radiation; optical energy gap.

Introduction

Solid polymer blends have been considerably studied in view of their wide potential application for novel systems and devices [1-3]. Suitable variation of preparing conditions like thickness, the electrical, electrochemical and optical properties of these materials could be selectively modified for particular properties in various applications [4-8]. It is well known that molecular structure and the physical properties of polymer could be modified by ionizing radiations [9,10]. Ionization of atoms and scission of molecules occur leading to the formation of charged species both ionic and free radicals. Raman scattering studies can provide information on the type of molecular species of the blends, while optical absorption studies are important to provide details of the electronic band structures, localized states and type of optical transitions, making these materials very attractive for chemical sensors in the detection of ionic species and for display panels[11-13].Several Poly Vinyl Chloride (PVA) blends containing chlorine have been investigated for possible use in dosimetry for measurement of radiation dose in γ-ray and electron beam facilities[14-16]. Treating substances with any form of electromagnetic radiation or high energy electrons is known as IRRADIATION. Electromagnetic radiation is essential for modern life. It includes X-rays, ultraviolet UV, visible light, infrared IR, and microwaves,. Recent advances in technology have brought about an increasingly important role for gamma rays and electron beams. Gamma irradiation of living species induces breaks in the DNA double helix preventing replication and hence sterilization, damage to polymers is by a similar mechanism.

In this article, we report the optical characteristics of PVC samples, which undergo change upon irradiation with Beta and X-rays.

Material and Method

The absorption coefficient α of dyed PVC samples was taken from the optical absorption spectrum using relation:

$$\alpha = 2.303A/d \quad \text{……………………………………………………………………………….(1)}$$

Where:
d = the sample thickness in cm
A = Defined by:

$A = \log (I_0 / I)$

Where, I_0 and I are the intensity of the incident and transmitted beams respectively. Analysis of optical absorption spectra could reveal the energy gap Eg between the Conduction Band (CB) and the Valence Band (VB) due to direct and indirect transitions of both crystalline and amorphous materials. The absorption edge coefficient α is a function of photon energy and obeys Mott and Davis's model (Mott and Davis):

$$(\alpha h\nu) = B(h\nu - E_g)^r \quad \ldots\ldots(2)$$

Where:

hν = The energy of the incidence photon

h = The Planck constant

E_g = The optical energy band gap

B = constant known as the disorder parameter which is nearly independent of the photon energy Parameter r is the power coefficient with the value that is determined by the type of possible electronic transitions, i.e., r = 1/2, 3/2, 2or 1/3 for direct allowed, direct forbidden, indirect allowed and indirect forbidden respectively[17,18]

The optical activation energy, E_e is the energy width of the tail of localized states in the band gap was valuated using the Urbach-edges method [19] given by the formula:

$$\alpha = \alpha_0 e^{h\nu / E_e} \quad \ldots\ldots(3)$$

Where (α_0) is constant and E_e is the width of localized states (the optical activation energy)of irradiated samples were determined from the slope of the straight lines of ln (α) versus photon energy (hν).

The optical behavior of materials utilized to determine its optical constants (refractive index (n), extinction coefficient (k), real and imaginary parts of dielectric constants (ε_1 , ε_2)). Several The extinction coefficients (imaginary part of the refractive index) can be calculated by the relation [20]:

$$k = \frac{\alpha \lambda}{4\pi} \quad \ldots\ldots(4)$$

The refractive index (n) can be measured (when the reflectance (R) and (k) are known) by using the equation [21]:

$$n = \sqrt{\frac{4R}{(R-1)^2} - k^2} - \frac{(R+1)}{(R-1)} \quad \ldots\ldots(5)$$

The complex index ($\overline{N}$) is given by [21]:

$$\overline{N} = n - ik = \sqrt{\varepsilon} \quad \ldots\ldots(6)$$

Where ε is the complex dielectric constant, given by:

$$\varepsilon = \varepsilon_1 - i\varepsilon_2 \quad \ldots\ldots(7)$$

The parameter ε_1 is the real part of dielectric constant; ε_2 is the imaginary part of dielectric constant, from equations (7) and (8) one can obtain:

$$\varepsilon_1 = n^2 - k^2 \quad \ldots\ldots(8)$$

$$\varepsilon_2 = 2nk \quad \ldots\ldots(9)$$

Experimental

The solution of PVC was prepared by dissolving 0.06 g in 10 mL of Tetrahydrofloride(THF) .The solution was stirred throughout temperature (323K)for 2 h and then left to cool. A 0.6 mL of the solution were added, and poured onto a horizontal glass plate and dried at room temperature for about 72 h. After drying, the films were peeled off and cut into several pieces, stored and ready for measurements. The average thicknesses of the films were found to be about 0.01, 0.0.15 cm. The irradiation was done in air at room temperature with beta and gamma radiation from Sr^{90} and Cs137sources the former emitted one photon while the later source emitted photons with average energy (0.662) MeV. The irradiation was carried out for two months; the obtained doses from both sources are 0.072 and 64 rad respectively.

The absorption spectra of the unirradiated and irradiated film were measured using UV-Visible spectrometer (Shimadzu, Model 1601) in the wavelength range 300-900 nm.

Results and Discussion

PVC samples were irradiated to doses up0.072 and 64 rad as result of expositing to beta and gamma sources respectively. Fig.1 shows the transmittance spectra in the wavelength range 300-900 nm of PVC for both. It is clear that the transmittance declare reduction (increases absorbance) with increasing of thickness and irradiation with beta and gamma rays moreover T decreases from 0.826 to 0.796 and to 0.711 and from 0.713 to 0.697 and to 0.655 for d=0.011 and 0.014cm respectively, this indicate that samples become more opaque or less transparent with expositing to both type of radiation ,this behavior reflects as an increment in n and k values as result of irradiation and thickness increasing (see table 1).the increasing of n values with thickness is ascribes to increasing of absorbance as mentioned before while the increasing of n values with expositing to both type of radiation is ascribes to crosslinking between polymeric chains take place as result of irradiation which causes increasing of molecular weight of polymer which intern increases n values[22] .

Reactions with radiation can be calcified into four categories:

1-Recombination -no change in properties,2-Crosslinking which causes increasing in strength and decreasing in elongation,3-Chain scission which causes loss of strength and elongation and 4-Combinations of all of the above. Plastics that crosslink more than they scission generally do better in the radiation environment ,it was found that highly crystalline polymers have higher resistance to radiation, 0n the other side if chain scission dominates then low molecular weight fragments, gas evolution (odour) and unsaturated bond (color) may appear.

Fig. 2&3 show wavelength dependence of n and k for both thickness of PVC samples unirradiated and irradiated with beta and gamma rays. Table (1) show that n increases from 1.86 to 2.42 for PVC films when t increases from0.0115 to0.014 cm, this behavior can be explained on the basic of that increasing of t leads to make PVC more dense (increasing packing density)which in turn decreases propagation velocity of light through them which resulting in increasing of n values since n represent the ratio of light velocity through vacuum to velocity through any medium .It is well known to say that when the material become more opaque to the incident light (as a result of increasing thickness)thus the velocity of light decreases and consequently n and k increases .

It clear that for lower thickness the dose sensitivity of the beta exceeds that of gamma rays i.e. the percentage increment of n with expositing to beta rays is higher than that with expositing to gamma rays, while for higher thickness the dose sensitivity of beta decreases i.e. the percentage increment of n with expositing to beta rays decreases while that of gamma rays remain constant , this ascribes to the fact that beta is electron beam while gamma is electromagnetic radiation. It was published previously that most thermoplastics like PVC experience a coulor shift after exposure to gamma radiation dose up 100 Gry[23], on the other hand highly amorphous materials (non crystalline) are generally resistant to radiation since the chain structure is capable of great ductility and they can tolerate many scissions without breaking up.

Figs.4 and 5 reveal the plot diagrams of wavelength dependence of ε_1, and ε_2 for PVC samples with different thickness unirradiated and irradiated with β and γ rays,it is concluded that the variation of (ε_1) mainly depend on the value of (n^2) because the smaller value of (k) comparison with (n^2) ,while the imaginary part of dielectric constant (ε_2) mainly depend on (k) values which are related to the variation of (α).The value of (ε_1)of unirradiated PVC obtained (at λ=500nm) in the transparent region i.e. the region beyond the absorption edge is listed in Table.1.

The optical absorption studies show that the direct optical energy band gaps and tail of extended states are dependent on dose and thickness. The absorption maximum which increases with of increasing thickness and doses this absorption corresponds to the excitation of outer electrons; provide information about the electronic transitions of the molecules in the samples. UV absorption is mainly due to electron (or anion) transitions from the top of the valence band to the bottom of the conduction band [18]. Analysis of optical absorption spectra could reveal the energy gap E_g between the Conduction Band (CB) and the Valence Band (VB) due to direct transitions of both thickness and irradiation type. The direct optical band gap can be evaluated from the linear plots of $(\alpha h\upsilon)^2$ versus hυ as illustrated in Fig.6&7for d=0.0115and0.014cm respectively at for both irradiation type .moreover the result show that when Eg decreases from 5.1 to 4.9 eV for t= 0.011cm and from 4.88 to 4.81eV when t= 0.014cm with expositing to beta and gamma rays respectively The results of E_e values for different doses(0.075for beta and 75 rad for gamma rays).are shown in Fig. 8.One can observe the contrast relation between E_g and E_e for lower thickness, the decreasing of the energy band gap (increasing of E_e)with increasing dose may be attributed to the increasing of structural disorder of the polymer films with increasing dose. The value of E_e is higher with the higher thickness. There has been reported the value of E_e for PVC films irradiated with electron beam was varied from 1.18-1.93 eV[18].

Poly (vinyl chloride) (PVC), is a degrading type of polymer and known to undergo extensive dehydrochlorination (resulting mainly loss of HCl) when exposed to energetic radiations like gamma rays, accelerated electrons, etc. The electrical conductivity of is known to increase when exposed to strong acids like HCl. Therefore onset and further enhancement of conductivity in the films prepared from PVC was observed when they are irradiated with ionizing radiations [23].

Conclusion

Increasing of thickness made PVC samples more opaque. Crosslinking is the dominate phenomena as a result of irradiation with β and γ rays. The sensitivity of gamma is thickness independent while the sensitivity of beta is thickness dependent. The shift in the optical band gap E_g values towards lower energy with radiation dose leads to a shift of the optical activation energy E_e value towards the lower energy region with increasing dose. The optical band gap (E_g) and the absorption edge decrease with increasing dose attributed to the structural disorder of polymer blends due to ehydrochlorination of trichloroacetic acid with increasing dose. The energy width of the tail of localized state in the forbidden band gap was evaluated using the Urbach-edges method. It was found that the activation energy (E_e) is less dependent of radiation dose but strongly dependent on the degree of disordered in polymeric samples. No change in color was observed for PVC films.

References

1.S. Preoneanu,., R. Torcu, M. Brie and G. Mihilesan, Mater. Sci. Forum, 191: 241-246,(1995).

2. M.Armand,, The history of polymer electrolytes. Solid State Ionics, 69: 309-319,(1994).

3.R. Koksbang, I. Olsen and D. Shackle, Review of hybrid polymer electrolytes and rechargeable lithium batteries. Solid State Ionics, 69: 320-335,(1994).

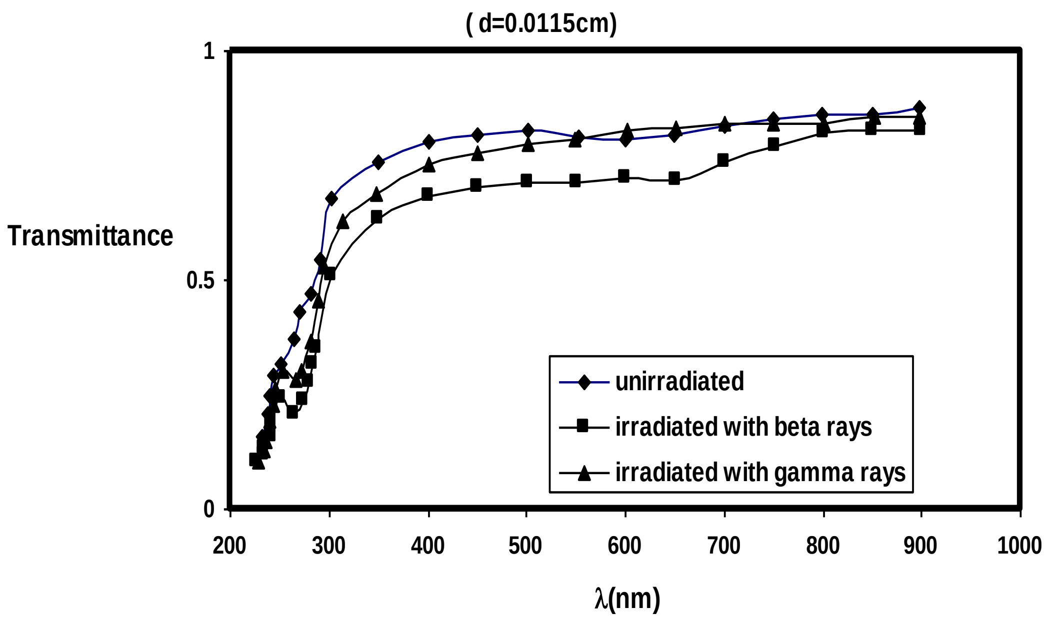
4.K. Abraham, and M.J. Alamgir, Electrochem. Soc., 137: 1657-1658,(1990)

5.A. Reiche, J. Tubke, K. Siury, B. Sander, G. Fleischer and S. Wartewig, 85: 121-127. *Am. J. Applied Sci., 6 (12): 2071-2077, 2009* 2077,(1996).

6. Reiche, A., T. Steurich, B. Sander, P. Lobitz and G. Fleischer, Characterization, mechanism and model Ion transport in gel electrolytes. Electrochim. Acta, 40: 2153-2157. DOI: 10.1016/0013-4686(95)00156-9,(1995).
7.B. Schartel,, J. Wending and J.H. Wendorff, Cellulose/poly (vinyl alcohol) blends. I. Influence of miscibility and water content on relaxations. Macromolecules, 29: 1521-1527. DOI: 10.1021/ma9506379,(1996).
8.R. Huq,, R. Koksbang, P.E. Tonder and G.C. Farrington, Electrochim. Acta, 37: 1681-1684,(1992).
9.A. Kovacs, M. Baranyai and L. Wojnarovits, Radiat. Phys. Chem., 57: 691-695. DOI: 10.1016/S0969-806X(99)00435- 1,(2000).
10.M. Barakat, K. El-Salamawy, M. El-Banma, M. Abdel Hamid and A. Abdel-Rehim Taha, Radiat. Phys. Chem., 61: 129-136. DOI: 10,1016/S0969- 806x(01)00181-5,(2001).
11.N. Aleshin,., N.Mironkov, A. Suvarov, J. Conklin, J.M. Su and R.B. Kaner, Phys. Rev. B: Condens. Matter, 54: 11638-11643. DOI:
10,1103/Phys. Rev B.54.11638,(1996).
12.K.. Ogura, K., T. Saino, M. Nakayama and H. Shiigi, J. Mater. Chem., 7: 2363. DOI: 10. 1039/a 7054639,(1997).
13.C. Devi, A. Sharma and V. .Rao, Mater. Lett., 56: 167-174. DOI: 10,1016/S0167-577x(02)00434-2,(2002).
14.A. Abdel-Fattah, A.A., M. El-Kelany and A. Abdel- Rehim, Development of radiation sensitive indicator. Radiat. Phys. Chem., 48: 497-503. DOI: 10. 1016/ 0969-806x(96)00014-x,(1996).
15. Abdel-Fattah, M. El-Kelany, F. Rehim and A. El-Miligy, J. Photochem. Photobiol. A: Chem., 10: 291-297. DOI: 10.1016/S1010- 6030(97)00195-0,(1997).
16.A. Abdel-Fatah, and M. El-Kelany, Radiat. Phys. Chem., 51: 317-325. DOI: 10. 1016/s0969-806x(97)00258-2,(1998).
17.K..Al-Ani, , I.H. Al-Hassany and Z..Al-Dahan, J. Mater. Sci., 30: 3720-3729. DOI: 10.1007/BF 00351890,(1995).
18. Arshak, A. and O. Korostynska, Sensors, 2: 347-355. DOI: 10.3390/s20800347,(2002)
19. N.Mott, and E. Davis, Electronic Process in Non-crystalline Materials. 2nd Edn., 604,(1979).
20.W.Klopffer ," Introduction to Polymer Spectroscopy",Springer – Verlag, (1984).
21.J.L.Pankov, Optical Process in Semiconductors, London(1971).
22. S. Bhateja , "J. Appl. Polm. Sci," 28,p 861,(1983).
23. H.BODUGOZ,,U.SEVIL, O.GÜVEN, Macromol. Symposia, 169 89-94, (1998).

Table 1.Illustats the values of n, ,k ,€$_1$, €$_2$,at ƛ=500nm, E_g, and E_e for PVC films prepared with different thickness unirradiated and irradiated with β and γ rays.

Thickness (cm)	Irradiation Type	n	kx10^{-4}	€$_1$	€$_2$x10^{-4}	E_g (eV)	E_e (eV)
0.0115	unirradiated Irradiated with beta rays Irradiated with gamma rays	1.86 2.20 1.96	0.66 0.79 1.18	3.47 4.85 3.84	2.47 5.21 3.11	5.10 5.00 4.90	1.649 1.736 1.550
0.014	unirradiated Irradiated with beta rays Irradiated with gamma rays	2.24 2.31 2.34	1.03 1.14 1.20	5.01 5.32 5.49	4.95 5.27 5.64	4.90 4.88 4.81	2.243 2.105 2.288



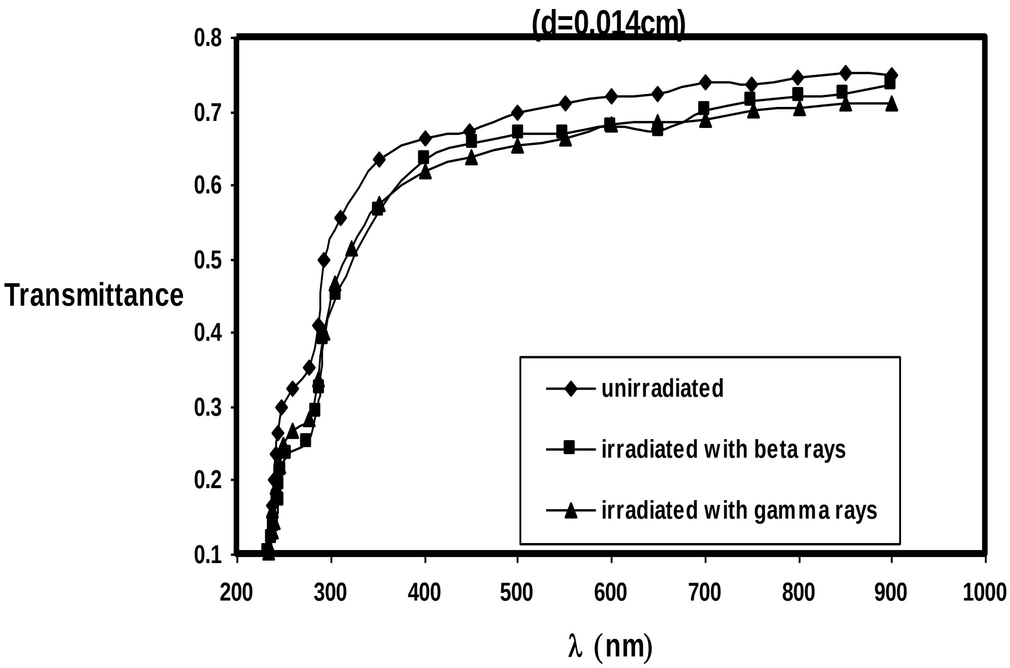
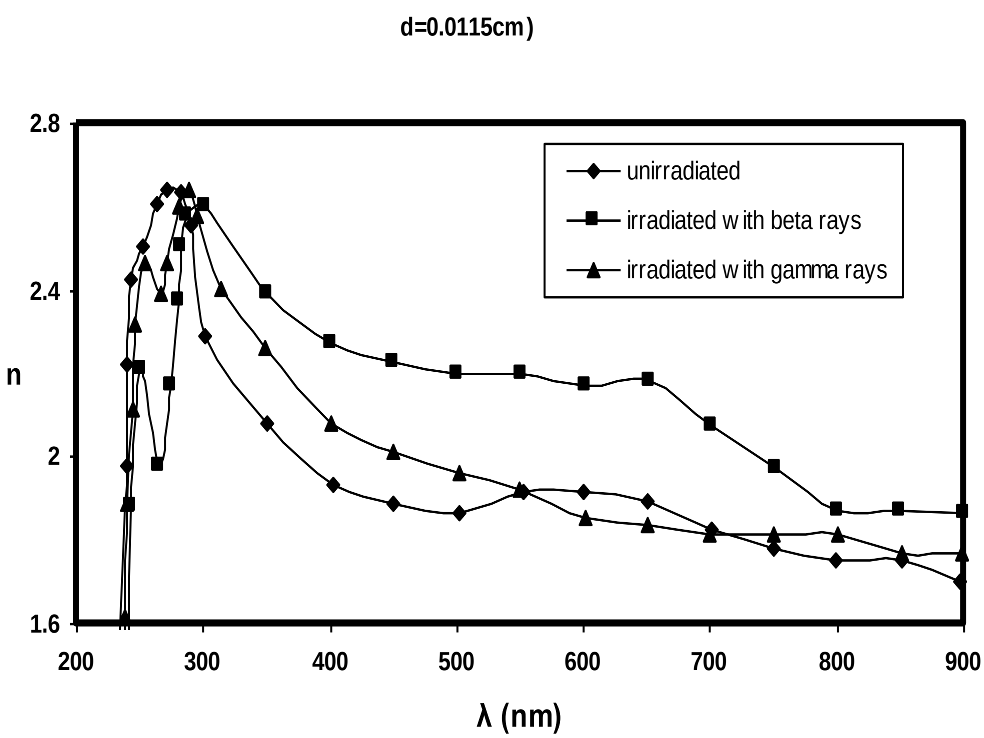


Fig.1 Transmittance spectrum of PVC films with different thickness unirradiated and irradiated with beta and gamma rays.



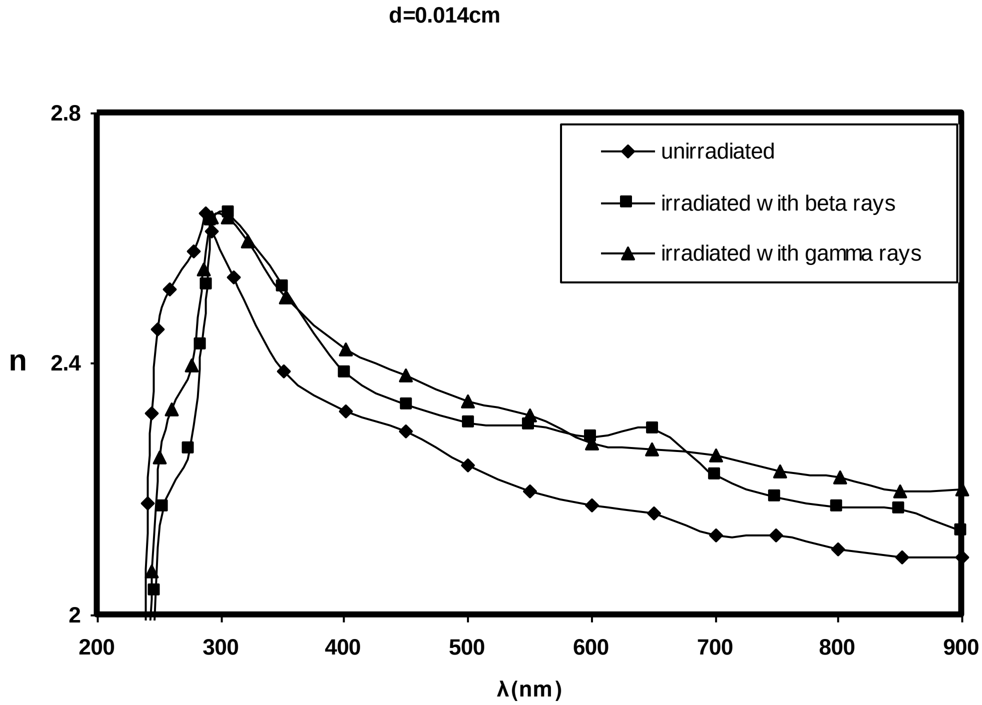
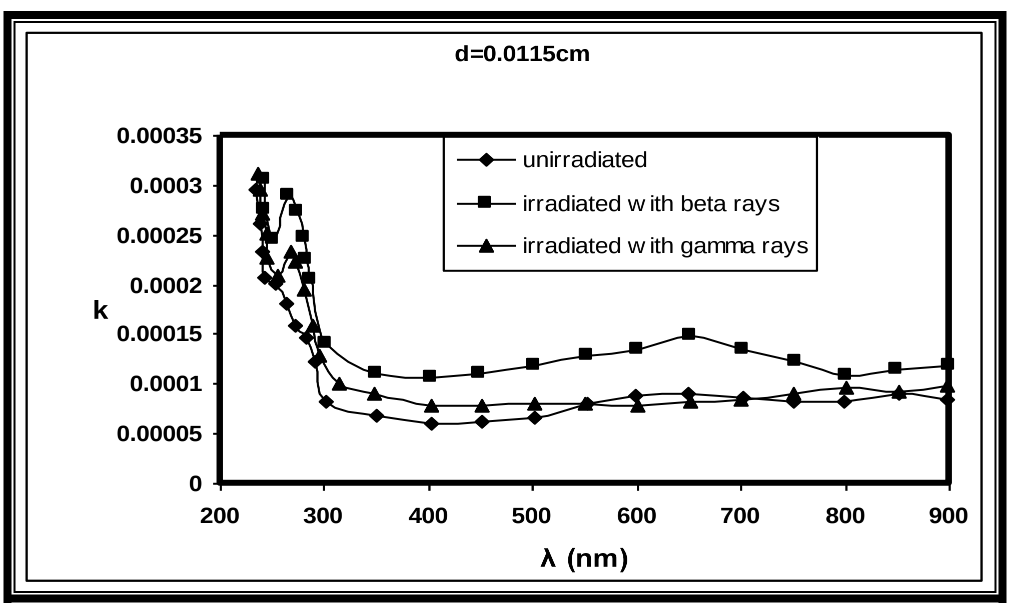


Fig.2 Variation of n with wavelength of PVC films with different thickness unirradiated and irradiated with beta and gamma rays.



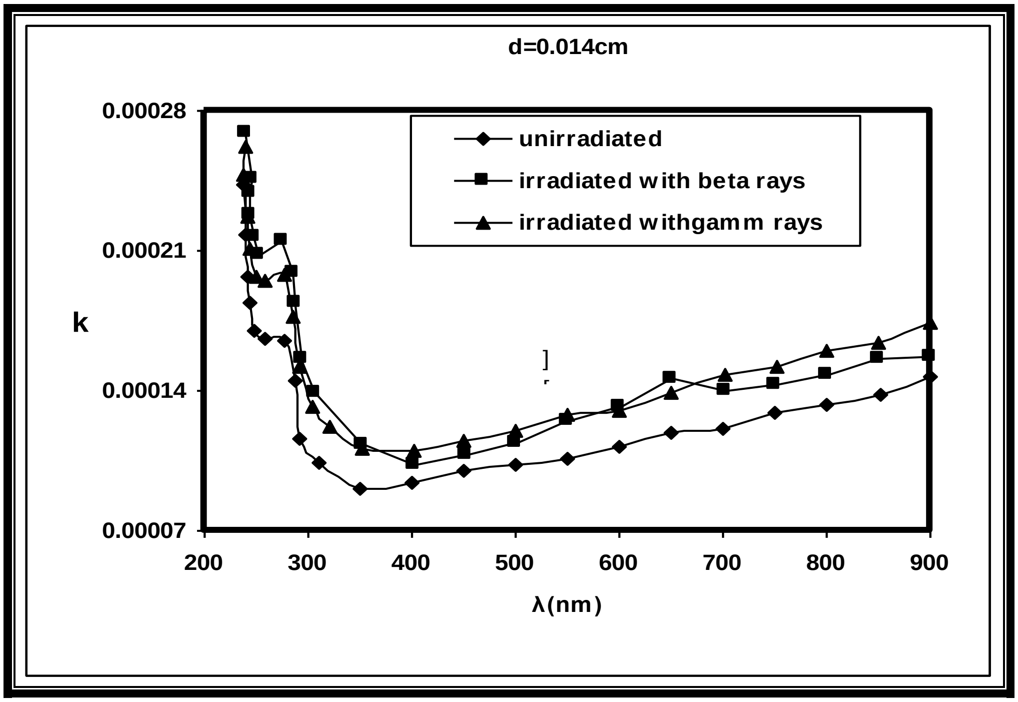


Fig.3 Variation of k with wavelength of PVC films with different thickness unirradiated and irradiated with beta and gamma rays.

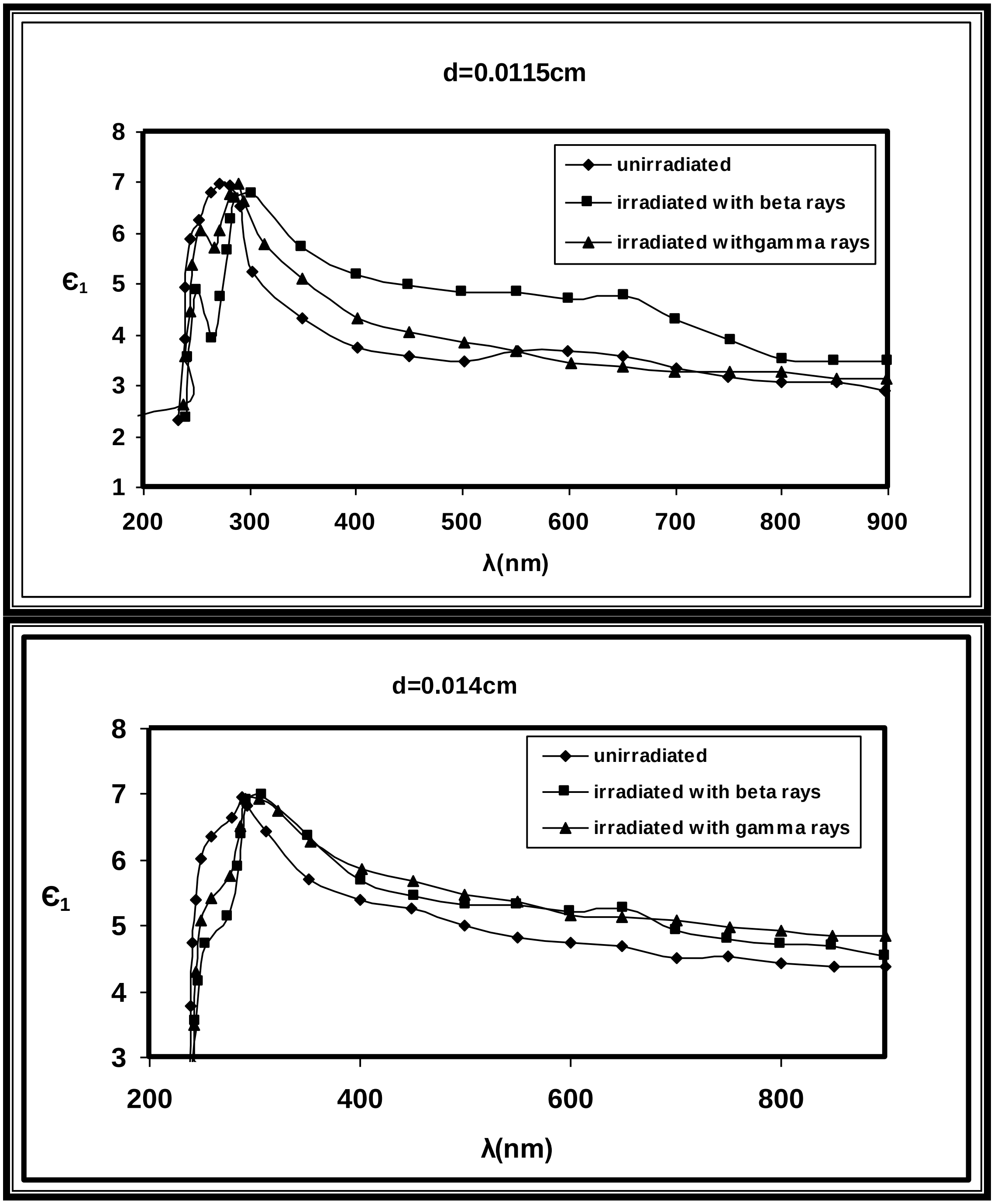


Fig.4 Variation of ε_1 with wavelength of PVC films with different thickness unirradiated and irradiated with beta and gamma rays.

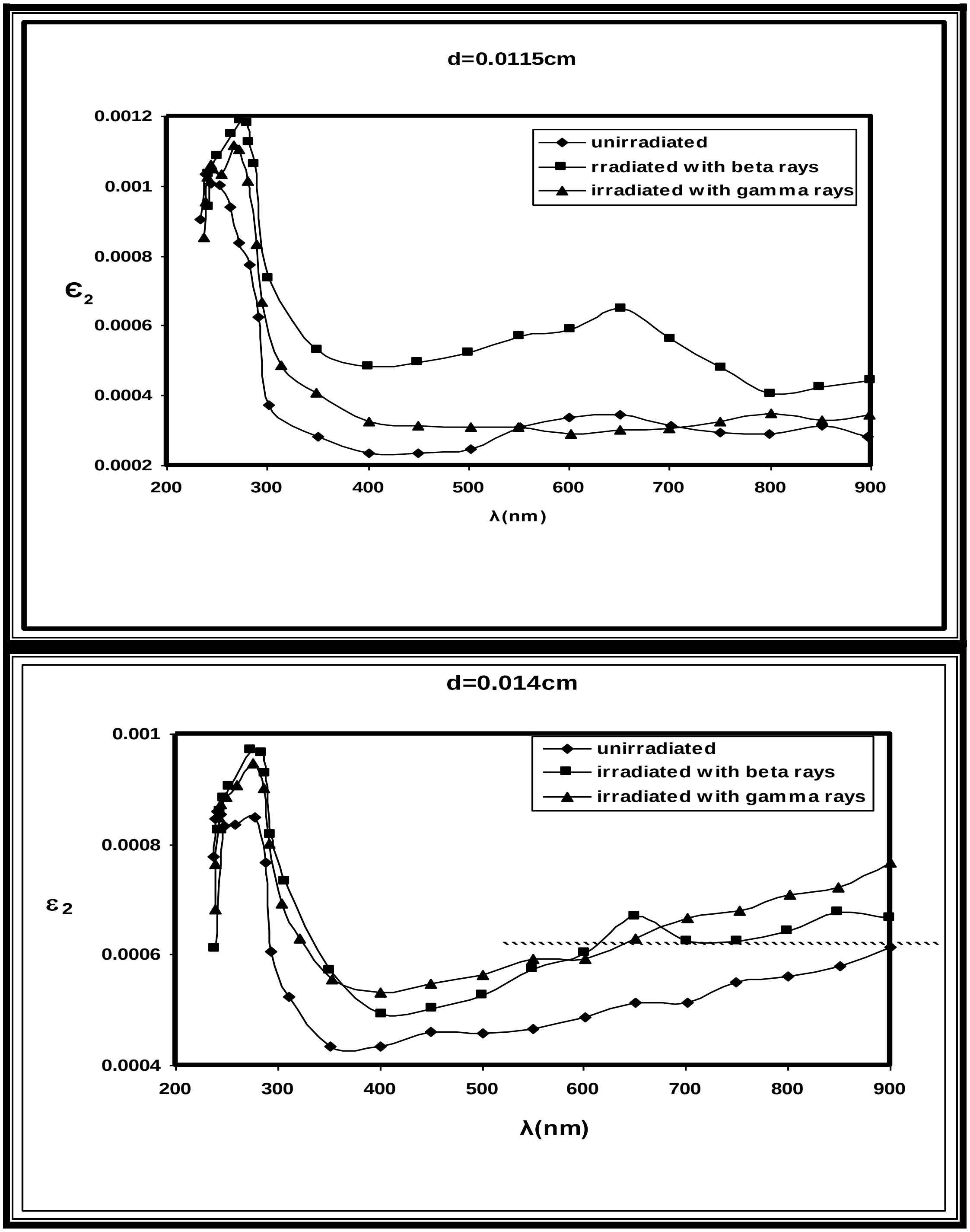
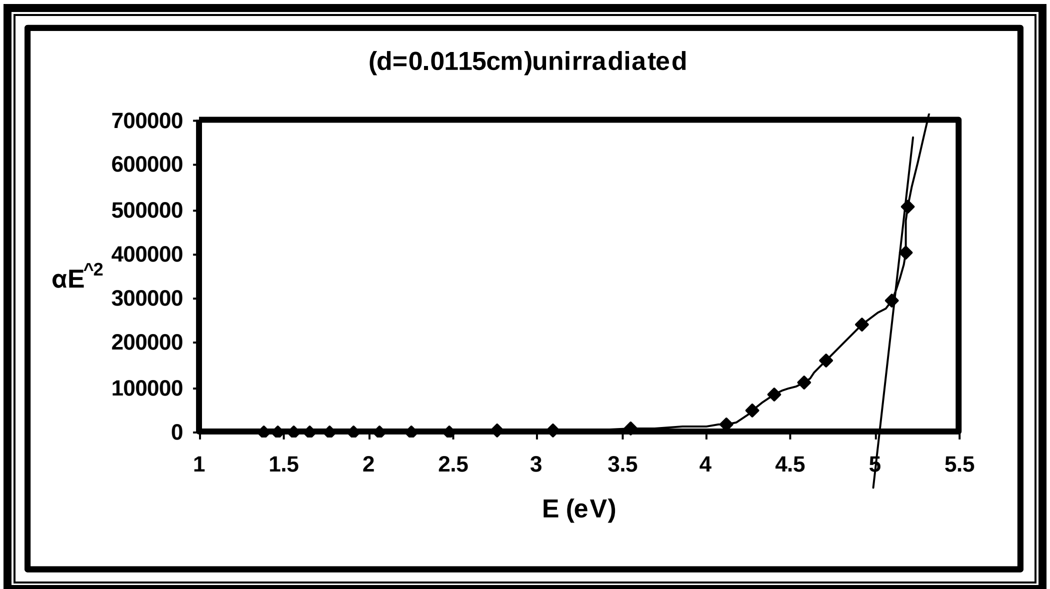
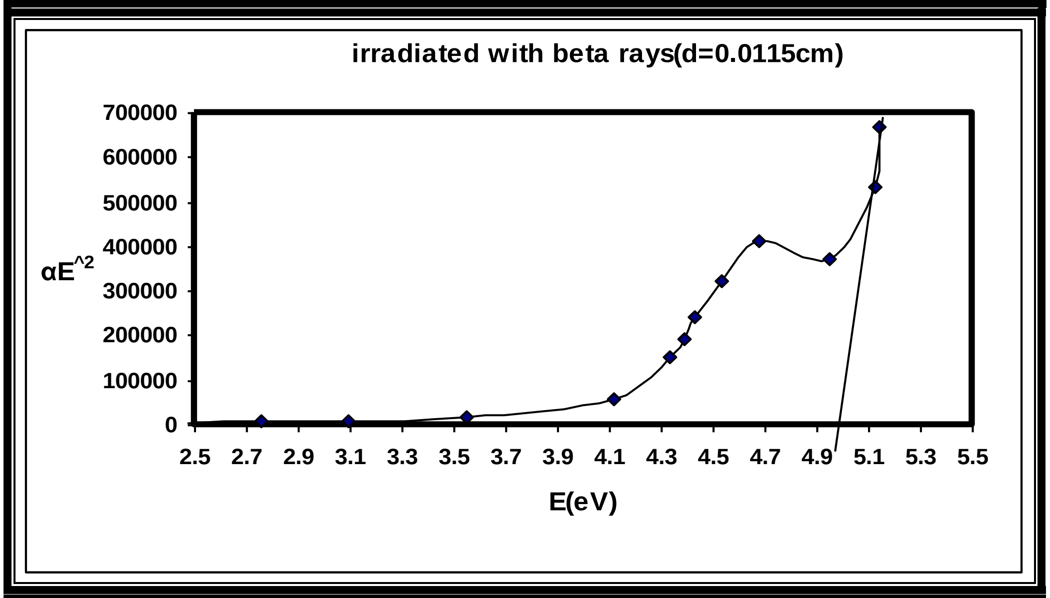


Fig.5 Variation of ε_2 with wavelength of PVC films with different thickness unirradiated and irradiated with beta and gamma rays.


(d=0.0115cm)unirradiated
αE^2
700000
600000
500000
400000
300000
200000
100000
0
1
1.5
2
2.5
3
3.5
4
4.5
5
5.5
E (eV)


irradiated with beta rays(d=0.0115cm)
αE^2
700000
600000
500000
400000
300000
200000
100000
0
2.5
2.7
2.9
3.1
3.3
3.5
3.7
3.9
4.1
4.3
4.5
4.7
4.9
5.1
5.3
5.5
E(eV)

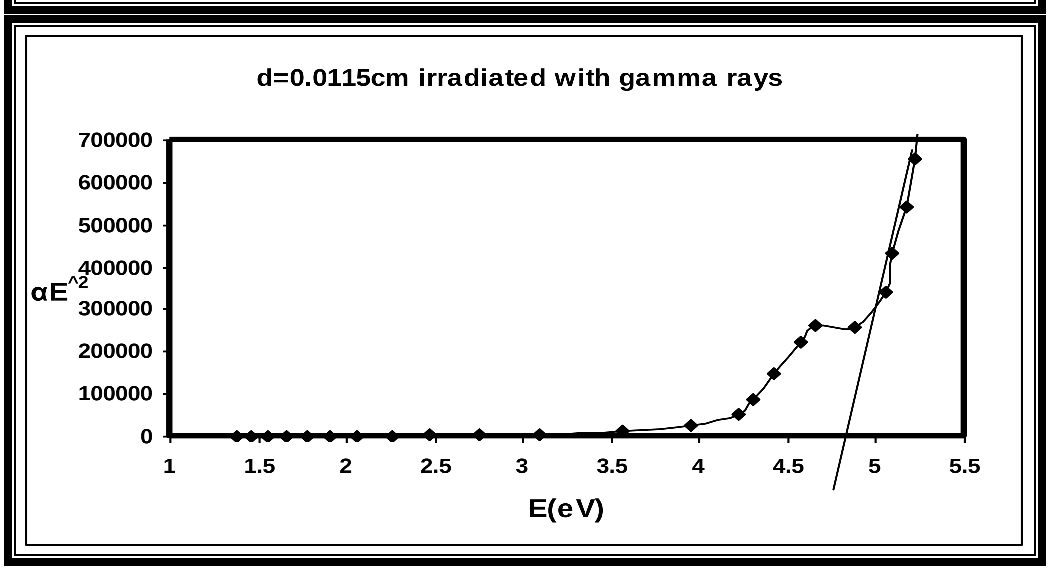
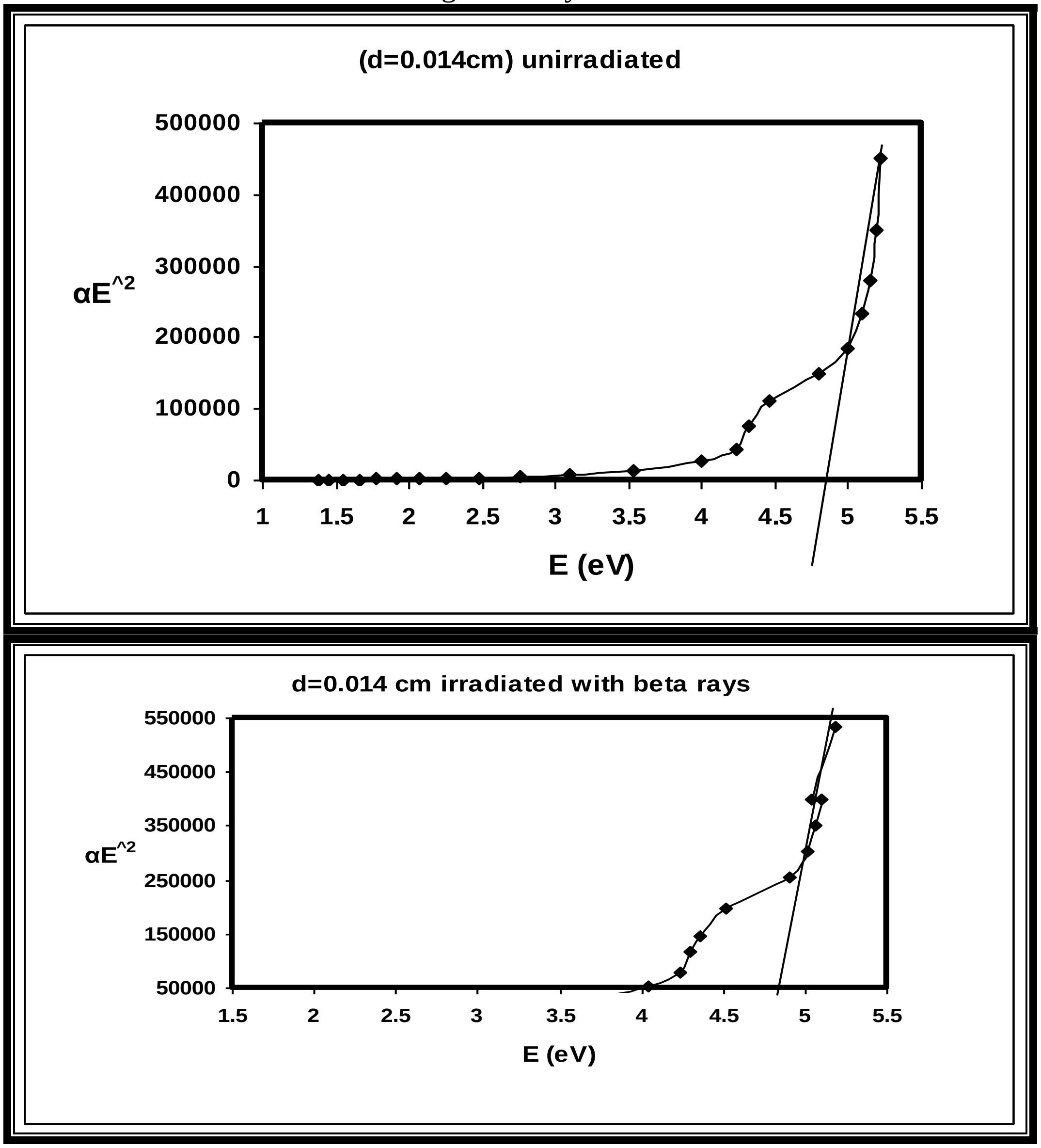

d=0.0115cm irradiated with gamma rays
αE^2
700000
600000
500000
400000
300000
200000
100000
0
1
1.5
2
2.5
3
3.5
4
4.5
5
5.5
E(eV)

Fig.6 Variation of $(\alpha h\nu)^2$ with energy of PVC films (d=0.0115cm) unirradiated and irradiated with beta and gamma rays.



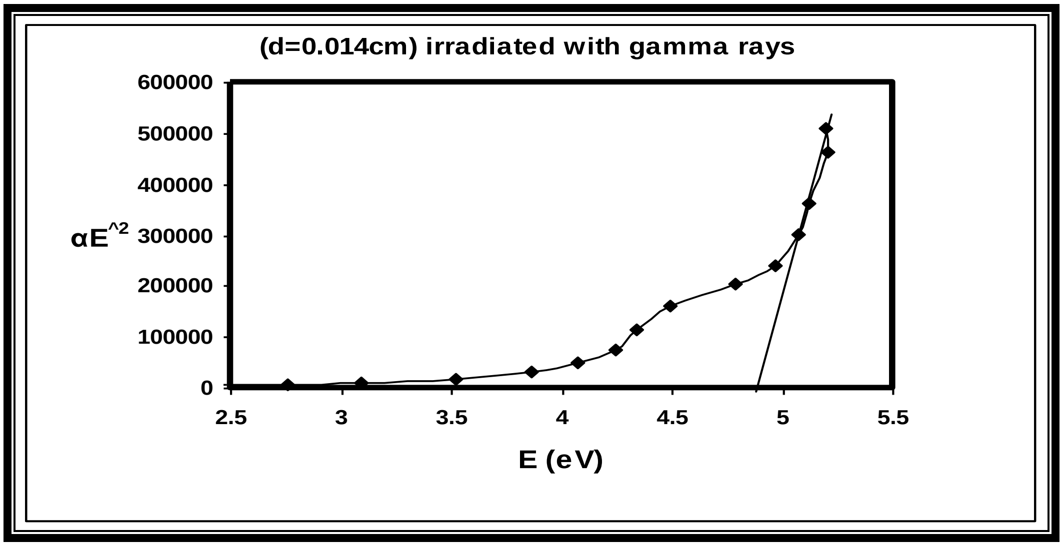
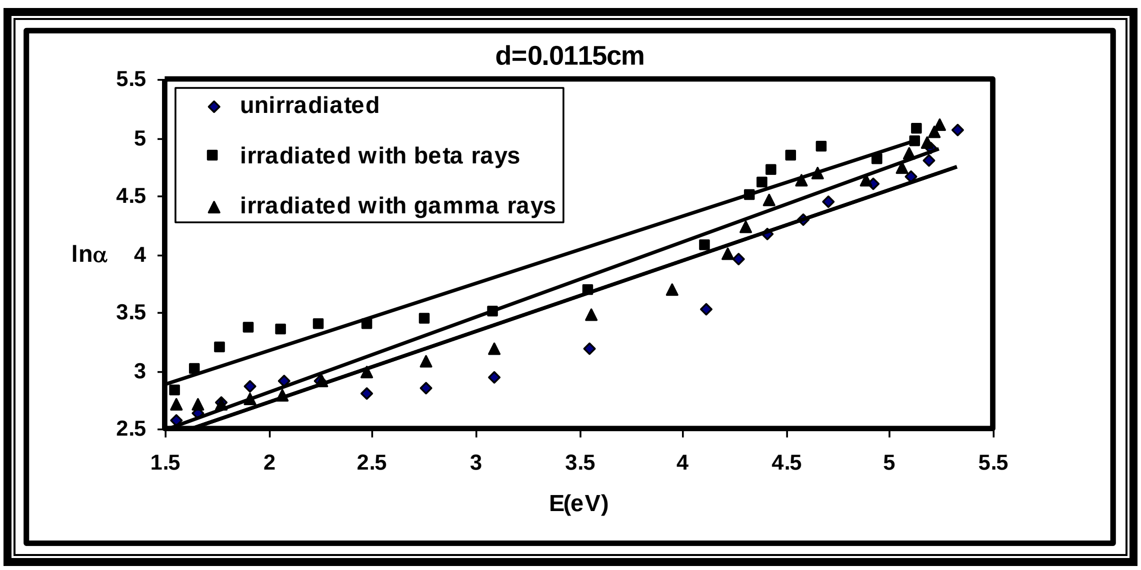


Fig.7 Variation of $(\alpha h\nu)^2$ with energy of PVC films (d=0.014cm) unirradiated and irradiated with beta and gamma rays.



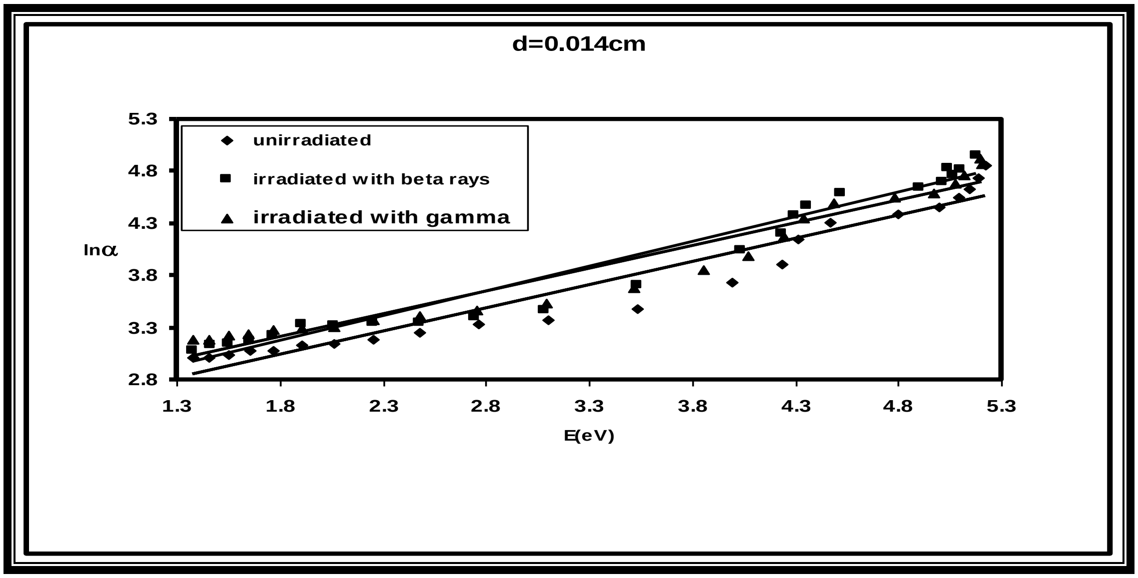


Fig.8 Variation of lnα with energy of PVC films with different thickness unirradiated and irradiated with beta and gamma rays.